EFFECT OF COBALT AND ZINC PRECURSOR LOADING ON THE CATALYST ACTIVITY OF FISCHER TROPSCH SYNTHESIS

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ABSTRACT

Five samples of Co-Zn/SBA-15 catalysts were prepared using wet impregnation method with different composition of cobalt loading (5, 10 and 15 wt % Co) and zinc loading (5, 10 and 15 wt % Zn) and were investigated with respect to physical and chemical properties as well influence on activity and selectivity for conversion of H_2/CO_2 synthesis gas. The catalysts were tested by using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), N_2 Adsorption Analysis (BET) and Thermogravimetric Analyzer (TGA). The feed gas of CO_2 instead of CO also had been considered that contributed to product selectivity since cobalt catalyst do not exhibit significantly in Water Gas Shift (WGS) activity and CO_2 neither formed nor produced during Fischer Tropsch (FT) synthesis with cobalt catalyst and H_2/CO. An investigation of catalytic CO_2 hydrogenation into high quality fuels and valuable hydrocarbons was carried out in a glass borosilicate reactor. The operating condition for catalytic testing is at 220 °C and 1 bar using H_2/CO_2 feed ratios of 3:1. Selectivity of products was depending upon the amount of metal loading constituent as well as the syngas mixture that used. It was found that higher metal loading with optimized promoter loading was the best catalyst for Fischer Tropsch synthesis. It is experimentally found that from the result of gas chromatograph, the conversion of CO_2 and product selectivities were calculated. The most efficient catalyst for Ficher Tropsch synthesis is 15% Co/10% Zn-SBA-15. This result was proven by the characteristic of catalyst which is the existance functional groups of cobalt oxides, Si-O-Si, Si-CH3, zinc oxide, OH band, Si-C, and others, higher intensity that indicates higher cobalt dispersion, possess large surface area as well as pore size, small weight loses that indicate thermal stability and having large number of catalyst particles attaching closely with one another that make it more effective during FT process.

ABSTRAK

Lima sampel Co-Zn/SBA-15 pemangkin disediakan dengan menggunakan kaedah impregnasi lembap yang mempunyai komposisi kobalt (5, 10 dan 15%) dan zink (5, 10 dan 15%), seterusnya meneliti pengaruh sifat fizikal dan kimia ke atas aktiviti pemangkin dan selektiviti bagi proses penukaran gas sintesis H_2/CO_2. Pemangkin telah dianalisa dengan menggunakan Spektroskopi inframerah transformasi Fourier (FTIR), Pembelauan Sinar-X (XRD), Pengimbasan Mikroskop Elektron (SEM), N_2 Analisis Penjerapan (BET) dan analisa Termogravimetri (TGA). Gas yang digunakan ialah CO_2 menggantikan CO juga telah dianggap sebagai penyumbang kepada selektiviti produk berikutan pemangkin kobalt tidak berperanan dalam proses perubahan gas menjadi air (WGS), aktiviti dan akibat penghasilan CO_2 semasa sintesis Fischer Tropsch (FT) dengan pemangkin kobalt dan H_2/CO. Suatu penyiasatan penghidrogenan CO_2 sebagai pemangkin kepada bahan api yang berkualiti tinggi dan hidrokarbon yang berharga telah dijalankan menggunakan reaktor borosilikat kaca. Parameter yang digunapakai untuk experimen ini adalah pada 220 ° C dan 1 bar yang menggunakan nisbah H_2/CO_2 iaitu 3:1. Penghasilan produk bergantung kepada jumlah juzuk muatan logam serta campuran komposisi gas yang digunakan. Ia mendapati bahawa muatan logam yang lebih tinggi dengan muatan penganjur yang optimum adalah pemangkin terbaik sesuai untuk sintesis Fischer Tropsch. Hasil uji kaji daripada gas kromatografi, penukaran CO_2 dan selektiviti produk dapat ditentukan. Pemangkin yang paling berkesan untuk sintesis Tropsch Ficher adalah 15% Co/10% Zn-SBA-15. Keputusan ini telah dibuktikan melalui ciri-ciri pemangkin yang wujudnya kumpulan oksida kobalt, Si-O-Si, Si-CH3, zink oksida, OH band, Si-C, dan sebagainya, beintensiti lebih tinggi yang menunjukkan bahawa penyebaran kobalt yang lebih tinggi, mempunyai kawasan permukaan yang besar serta saiz liang, kehilangan berat yang sedikit menunjukkan kestabilan terma dan mempunyai sejumlah besar zarah pemangkin yang bersusunan rapat antara satu sama lain yang membuat ia lebih berkesan semasa proses FT.

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LIST OF ABBREVIATION

BET	N_2 Adsorption Analysis
Co	Cobalt
Co_3O_4	Cobalt oxide
FT	Fischer Tropsch
FTIR	Fourier Transform Infrared Spectra
GTL	Gast to Liquid
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
WGS	Water Gas Shift
XRD	X-Ray Diffraction
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

The increasing demand for high quality and environmentally friendly in transportation fuels together with the technology improvements in gas-to-liquid (GTL) processes making them more efficient and cost competitive. This latest innovation of technology has renewed the interest of using natural gas as a potential source of hydrocarbons (Fleisch, 2002). Often, in remote location of oil fields, a considerable amount of natural gas can be found, where the pipeline to transport the gas is not economically available. This condition has led natural gas to be flared, vented, or pumped undergrounds (Thayer, 2000). Therefore, the need to find an efficient process for utilizing natural gas receives considerable attention.

GTL is a technology that converts the gas (natural gas, biomass, and coal) to liquid fuel for easy to transport (Wilhelm et al., 2001). GTL process consists of three stages which are synthesis gas generation, production of heavy-chain hydrocarbons by Fischer-Tropsch synthesis and heavy fraction hydrocracking for production of useful products such as naphtha, lubricants and diesel (Aguiar et al., 2005). Particularly, diesel fuels made with GTL technology undergoes the Fischer Tropsch (FT) synthesis process offers significant environmental and efficiency benefits over those derived from crude oil, as they are mainly composed by liner paraffins having high cetane numbers as

higher cetane number gives higher speed diesel operation as well as free of sulfur and aromatics pollutants (Van der Laan and Beenackers, 1999). FT synthesis products have been practically used in worldwide as the alternative fuel to replace conventional diesel fuel in transportation by using syngas instead of crude oil which the source becomes crucial. The production process to obtain the FT synthesis product can be described as in Figure 1.1

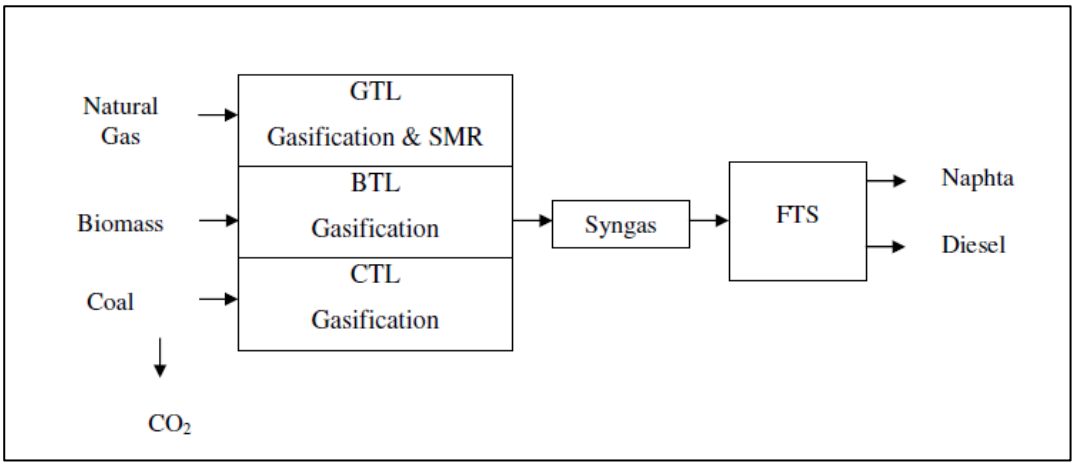

Figure 1.1: Potential routes to clean liquid fuels based on the Fisher Tropsch synthesis process (Wilhelm et al., 2001).

Fischer Tropsch (FT) synthesis proceeds through a polymerization-type mechanism where monomeric CH_3 species coming from the catalytic dissociation and hydrogenation of CO_2 are assembled in successive CH_3 insertion straight chain species (Brady and Pettit, 1980). The nature of product site requirements to selectively direct the CO_2 hydrogenation toward specific products and the structural and chemical changes experienced by the metal catalyst under working conditions (temperature of 200-350^{o}C, relatively high pressures, CO_2-rich environment and present of the by-product (Wilson, 1995).

The common catalyst that has been used in Fischer Tropsch industrial is metal that categorized as transition metals in group VIII. Their noticeable activities in the hydrogenation of carbon dioxide to hydrocarbon are greater than other metal group. The most active metals that used in catalytic conversion of syngas are ruthenium, iron,

nickel, and cobalt with the decreasing active metal. However, cobalt is the more suitable because it is more resistant to deactivation and cheaper that ruthenium which ruthenium reserves are insufficient for large scale industry. Cobalt supported on oxide supports is generally more resistant to attrition than iron precipitated counterparts as they are more suitable for use in slurry reactor. In addition, cobalt gives higher conversion of syngas due to large pore size that provide more surface area (Khadakov et al., 2007). Table 1.1 shows the detail comparison between cobalt catalyst and iron catalyst which are the common catalysts being used in industry.

Table 1.1: Comparison between Cobalt and iron catalysts in FT synthesis (Khadakov et al., 2007)

Parameter	Cobalt	Iron catalyst
Cost	More expensive	Less expensive
Lifetime	Resistance to deactivation	Less resistance to deactivation
Activity at low conversion	Comparable	Comparable
Productivity at high conversion	Higher, less significant effect of water on the rate of conversion	Lower, strong negative effect of water on the rate of carbon
Maximum chain growth probability	0.94	0.95
Maximum sulphur content	<0.1 ppm	<0.2 ppm
Flexibility (temperature and pressure)	Less flexible, significant influence of temperature and pressure on hydrocarbon selectivity	Flexible, methane selectivity is relatively low even at 613K

On the other hand, the process also demonstrated that the larger pore size enhanced the activity and selectivity to C5+ products in the Fischer-Tropsch reaction on cobalt catalysts supported on periodic mesoporous silicas (SBA-15) (Khodakov et al.,2002). In this respect, SBA-15 metal displaying larger pore size which is 2–50nm in

diameter. The use of periodic mesoporous silica (SBA-15) as a Fischer-Tropsch catalyst support has witnessed a tremendous growth. The high surface area (500 - 1500 m^2/g) of the SBA-15 gives higher metal dispersions due to providing more active sites. The dispersion gave better result after an amount of promoted noble metal zinc was promoted to the cobalt catalyst. It permits better control of the cobalt particle size and the distribution of hydrocarbon products from the FT synthesis. Thus, the best choice to recommend is SBA-15 as the catalyst to get higher catalytic activity and hydrocarbon selectivity in FT synthesis for cobalt based catalyst and Zn as promoter.

Fischer Tropsch synthesis is producing mostly fuel type products which are based on number of carbon such as wax, diesel, gasoline, naphtha, LPG and kerosene. But our main products are combined diesel and gasoline after product upgrading separation. But then, F-T synthesis is producing such as products below after going further to product upgrading section. Figure 1.2 shows the percentage of Fischer Tropsch product.

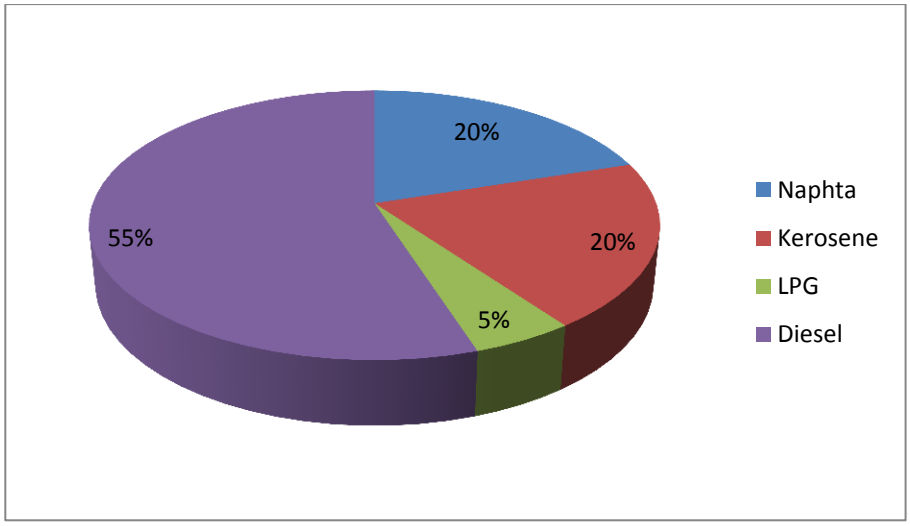

Figure 1.2: Percentages of the GTL products (Shalchi, 2006).

There are many factors that contribute on impact of the percentage of the either product increases or decreases. The percentage is rise or decline depending to the kind of technology employed nature of the catalyst, and the conditions of the reactions used. The properties of the GTL products are typical with respect of its combustion or its

environmental effects. Hence the important care of the properties of the products play a great part in the promotion of the GTL industry (Shalchi, 2006).

1.2 Problem Statement

The development of new catalysts is the necessity to improve better, cleaner manufacturing processes for the multitude of fine chemicals for daily life (Weitkamp, 2000). Catalyst is a vital part of any industrial Fischer Tropsch process. The synthesis products become highly demanded since the fuels are eco-friendly products which contain almost no sulphur. Several recent studies have revealed the feasibility of conversion of syngas into products of higher added values such as olefins, aromatics and oxygenous derivatives .These routes are possible if the reaction is carried out over a optimize catalyst.

In the industry application, iron, cobalt and ruthenium are the common catalysts for FT synthesis (Mukaddes, 2005). However, cobalt catalyst is being the preferred catalysts due to its high activity for FT synthesis, high selectivity to linear hydrocarbons, low activity for the water gas shift reaction, more stability toward deactivation by water and low cost compared to Ru (Tavasoli et al., 2007).

The application of SBA-15 which categorized in mesoporous silicas functions as a supports to the cobalt base catalysts. It has been chosen because the pores have very high surface area that will permit high dispersions at higher cobalt loading as compared to other silicas (Martinez et al., 2003).

Cobalt catalyst that promoted by noble metal like zinc has given strong impact on the catalyst structure and dispersion as well as FT reaction rates (Khodakov, 2009). Zinc promoter is used in this research in order to improve the reduction and reactivity of cobalt catalysts. In addition, it was commonly used in industry for hydrocarbon synthesis due to its lower price than other.

Numerous studies have shown that the catalytic conversion of syngas mixture into liquid hydrocarbons can be proceeding with high content of CO_2 in feed gas. Weatherbee et al. proposed that CO_2 hydrogenation process has follow the same reaction pathway with the formal process which is CO hydrogenation but different in product selectivity. So in this research, the investigation is about to see the how CO_2 affected the catalytic process that later will gives a large effect to the hydrocarborns produced.

1.3 Objective of Research

The objectives of this research are as follows:

- To prepare SBA-15 as supporter and to synthesis Co-Zn/SBA-15 with different cobalt and zinc loading
- To characterize of synthesized catalysts with different composition of cobalt and zinc loading by using several analytical techniques.
- To evaluate the effect of cobalt and zinc loading precursor on catalyst activity and product selectivity with influence of CO_2 fed.

1.4 Scope of Research

In order to accomplish the objectives, scopes of research have been identified in this research to manage the task within the frame work. The scopes of this research are divided into three. Firstly, synthesizing the optimize catalyst for FT synthesis which is SBA-15. The influence of different loading of cobalt and zinc precursor was investigated after synthesize Co-Zn/SBA-15 catalysts with different cobalt and zinc loading which range 5 to 15 wt% using incipient wetness impregnation method. The catalysts were then characterized for their properties by using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Thermogravimetric Analyzer (TGA) Scanning electron microscope (SEM), and N_2 adsorption analysis (BET). Lastly, the

catalysts have been tested in glass borosilicate reactor with furnace and connected to the online gas chromatograph to detect the hydrocarbon production and then analyzed the catalyst activity performance based on the selectivity.

CHAPTER 2

LITERATURE REVIEW

2.1 Gas to Liquid Process

Gas-To-Liquids (GTL) processes have received wide spread attention as an economically viable route to convert natural gas to ultra clean liquid fuels. Recently, there has been an increasing interest in the conversion of remote and abundant natural gas into high quality fuels and valuable raw chemicals via synthesis gas. The GTL is the process of converting natural gas into transportable liquids and consists of three main steps, (i) the reforming of synthesis gas, (ii) the production of hydrocarbons from synthesis gas through Fischer Tropsch synthesis, and (iii) the optimization to upgrade and separate products (Shikada et al., 1983). There are several key factors that drive growth in the GTL industry (Fleisch et al., 2002):

- The need to monetize the large amount of existing stranded natural gas reserves.
- The market demand for cleaner fuels and new cheaper chemical feed stocks.
- Technological development by existing and new role players which is leading to cost effectiveness of FTS technology from development of more active catalysts and improved reactor systems.
- Increased interest from gas-rich host countries.
- The need to diversify economies and to create new employment opportunities.

The synthesis gas manufacturing and the product upgrading rely on established technologies. Synthesis gas manufacturing is applied widely in the production of methanol and ammonia. Future developments are expected in the field of catalytic partial oxidation and in membrane techniques for oxygen purification (Venkatarama et al., 2000). Product upgrading processes directly originate from the refining industry and are highly optimized. The three steps in GTL are schematically represented in the block diagram of Figure 2.1.

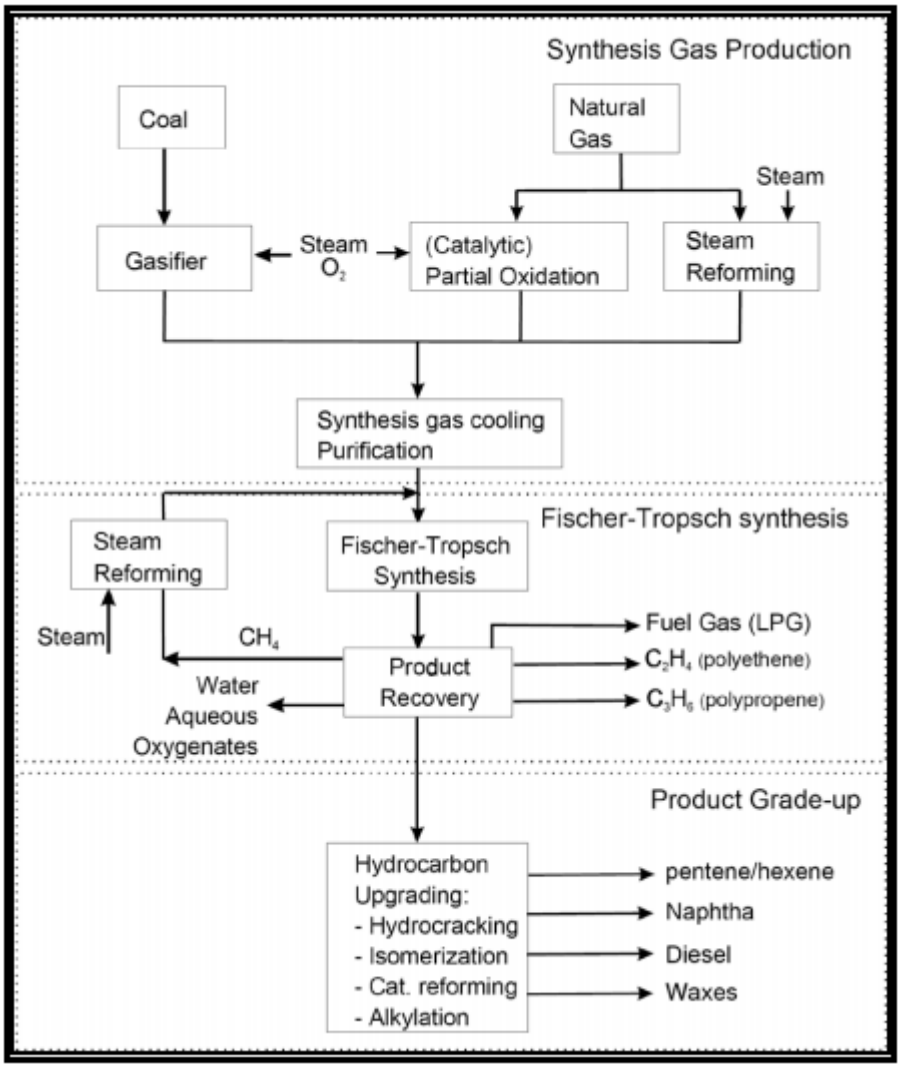

Figure 2.1: The main three processes present in Fischer-Tropsch synthesis (Tiefeng and Yong, 2007).

2.2 Synthesis Gas Manufacturing

Synthesis gas is a mixture of carbon monoxide (CO), carbon dioxide (CO_2) and hydrogen (H_2), which can be obtained from any carbon containing feedstock. Three basic methods of converting a feed stream into synthesis gas exist such as reforming, partial oxidation, and catalytic partial oxidation. Instead of natural gas, synthesis gas also can be produced by catalytic reaction or partial oxidation of fossil fuels such as coal, refinery residues, biomass or others. Table 2.1 below shows synthesis gas composition for different feedstock.

Table 2.1: Synthesis gas composition for different feedstock (De Smet, 2000)

Feedstock	Process	Component (vol%)			
		H_2	CO	CO_2	Other
Natural gas, steam	SR[1]	73.8	15.5	6.6	4.1
Natural gas, steam, CO_2	CO_2 - SR[2]	52.3	26.1	8.5	13.1
Natural gas, O_2, steam, CO_2	ATR[2]	60.2	30.2	7.5	2.0
Coal/heavy oil, steam	Gasification[1]	67.8	28.7	2.9	0.6
Coal, steam, oxygen	Texaco gasifier[1]	35.1	51.8	10.6	2.5
Coal, steam, oxygen	Shell/Koppers gasifier[1]	30.1	66.1	2.5	1.3
Coal, steam, oxygen	Lurgi gasifier[3]	39.1	18.9	29.7	12.3

SR= steam reforming, CPO= catalytic partial oxidation, ATR= autothermal reforming

In partial oxidation, the feed stream is mixed with steam and oxygen at high temperature (1573-1773 K). It is partially combusted followed by endothermic reforming steps and the water-gas shift reaction. Meanwhile, for the catalytic partial oxidation, a catalyst plays the function of the flame in the partial oxidation. The advantages of the catalytic partial oxidation of methane over steam reforming of methane are the low exothermicity of the process and the high reaction rates (De Smet, 2000).

2.3 Fischer-Tropsch (FT) Synthesis

Fischer-Tropsch synthesis is the process that converts synthesis gas that contains a mixture mainly of carbon monoxide, carbon dioxide and hydrogen, into a wide range of long chain hydrocarbons such as alkanes, alkenes, alcohols, aldehydes, ketones, ethers and acid as well as oxygenates (Gholami et al., 2009). Fischer-Tropsch synthesis provides alternative routes for the production of transportation fuels and petrochemical feedstock and it is the other way around to the classic refining of crude oil to produce the liquid fuel products.

Fischer Tropsch technology is seems to be increasing in these recent decades. The increasing importance of the Fischer-Tropsch synthesis for the near future is illustrated by four criteria:

- The world reserves of carbon-containing resources
- The geographic location of these reserves
- The demand for cleaner feedstock
- The reduction of CO_2 emissions.

The hydrocarbon and wax that produced by the low temperature FT process consists of linear paraffin with a small fraction of olefins and oxygenates. The FT mechanism is quite complex and it can be described in the following steps:

1) Initiation or C_1 compound formation.

2) Hydrocarbon chain growth by successive insertion of the C_1

3) Chain termination by: - desorption of unsaturated surface species, and

- Hydrogenation and desorption of saturated species.

The Fischer-Tropsch product spectrum consists of complex multi-component mixture of linear and branched hydrocarbons and oxygenated products. Main products are linear paraffin and α-olefins.

2.4 H_2/CO_2 Syngas

The synthesis gas or syngas that can be derived from coal, natural gas, or biomass primarily contains H_2, CO, and CO_2.The composition of syngas is reliant on many aspects such as gasifier type, operational conditions, and gasifying agents, causing the composition of CO_2 in the syngas varies from around 1 to 30% (Higman, 2007). Discharge control and utilization of CO_2 has received abundant of attention due to its large-scale availability and the harmful effect of carbon dioxide to the environment. Numerous approaches have been suggested to maintain the concentration of atmospheric CO_2 or to diminish and recycle it. Among these, the hydrogenation of CO_2 has conventionally been carried out on catalysts that are considered to be active and selective for the FT reaction (Rao et al., 1992)

The mechanism of CO_2 hydrogenation in FT synthesis is assumed to proceed in two steps; first, the reverse WGS (R-WGS) reaction takes place to produce CO, which is afterwards consumed in the FT conversion while the direct hydrogenation of CO_2 has also been suggested as an further reaction (Riedel et al., 2001) However, regardless of whether the conversion of CO_2 to hydrocarbons take place in one or many steps, the overall effect is that CO_2 is hydrogenated and being referred to the overall reaction as CO_2 hydrogenation. Figure 2.2 shows the mechanism of CO_2 hydrogenation that proposed in FT synthesis

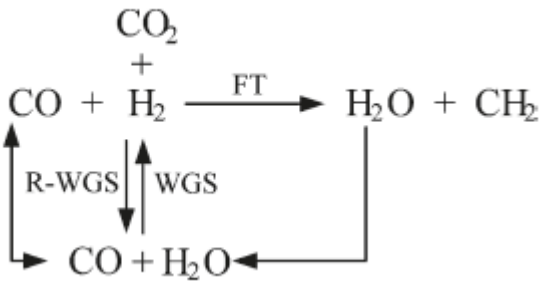

Figure 2.2: Reaction scheme proposed for H_2/CO or H_2/CO_2 feed gas for FT reaction (Riedel et al., 2001).

Cobalt based catalyst active in both WGS and R-WGS reactions would be ideal catalyst for use in the FTS for CO_2 syngas feeds. H_2/CO_2 can be converted into hydrocarbon products of a structure and composition similar to those obtained with H_2/CO over cobalt catalyst (Riedel et al., 2001). However, hydrogenation on cobalt-based catalysts shows that CO_2 hydrogenation has a higher selectivity for light hydrocarbon products with a low alpha distribution (Shi et al., 2005)

The CO_2 produced can be reduced by increasing the rate of the R-WGS reaction, with the potential addition of CO_2 as the WGS reaction is an equilibrium-controlled reaction. CO_2 creation could be significantly declined on cobalt catalysts when CO_2 was added to the syngas. The accumulation or recycling of CO_2 drops the net rate of CO_2 formation, and raises the fraction of the oxygen atoms in CO that are removed as H_2O. This is an essential practical concern when cobalt-based catalysts are used for H_2/CO mixtures derived from natural gas (Davis, 2007).

2.5 Fischer Tropsch Reactors

F-T reactor plays a main role in F-T plant which is considering the operating temperature, pressure and type of catalyst used. Currently there are three types of reactor that commercially used for FT synthesis. Figure 2.3 shows the schematic diagram of the reactor.

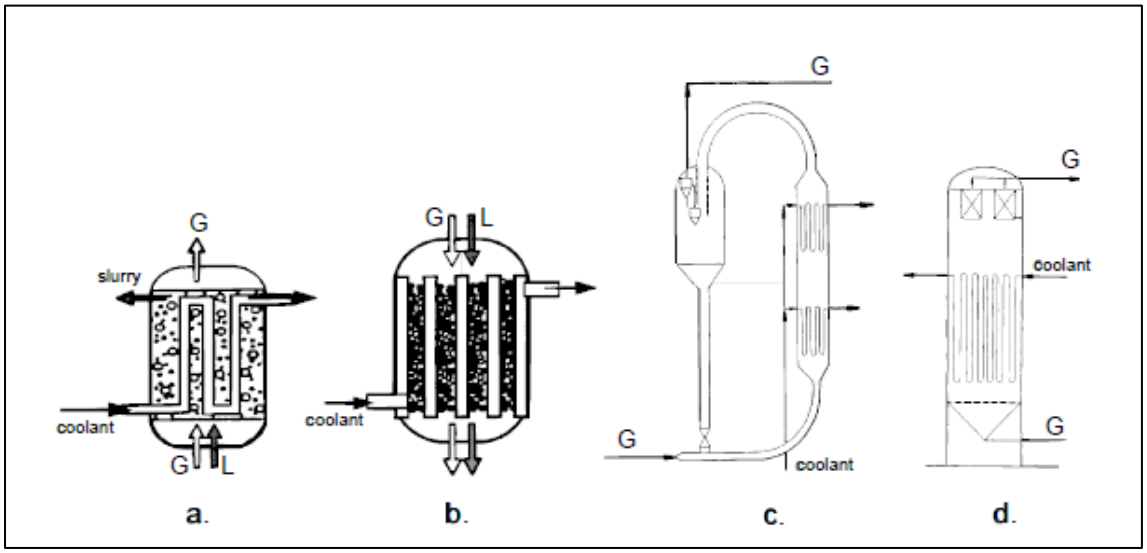

Figure 2.3: Possible reactors for Fischer-Tropsch synthesis a. Slurry bubble column reactor; b. Multi tubular trickle bed reactor; c. Circulating fluidized bed reactor; d. Fluidized bed reactor (Sie, 1998)

In a slurry-phase reactor, the feed syngas is bubbled through inert oil in which catalyst particles are suspended. Conversion by slurry-phase FT synthesis can achieve single-pass fractional conversion up to 80%. This compares to less than 40% conversion with traditional fixed-bed reactors. High single-pass conversion rates make slurry-phase reactors especially attractive from an overall cost perspective for operating temperature process designs. The slurry bed reactors operate in series and composed of 5 stages (Kreutz et al., 2008). The syngas is fed in the first stage of slurry bed reactors operating at 220ºC and 21.4 bars can be converted into higher linear paraffin over cobalt catalyst. The bubble column slurry bed reactor eliminates extensive heat, released by FT synthesis reaction via steam generation and provides significant advantages over conventional fixed tubular reactor and fluidized bed reactors.

Fluidized bed reactors are preferably suited for production of lower molecular weight long chain hydrocarbons from syngas. This reactor can operate only when all the reactants are in gaseous phase. Fixed fluidized bed reactor operates at a pressure at 24 bar and a temperature of 340ºC while circulating bed reactor runs at 330-350ºC and pressure of 25 bar. These types of reactor can be used for gasoline production. The chain growth probability (α) in fluidized bed reactor is less than 0.71 for stable bed

process since it is eliminating the production of heavy wax. For very high α, removal of hydrocarbon from the catalyst becomes a serious problem. Catalyst regeneration is frequent due to high condensable products in the fluidized bed process (Jager et al., 1996).

From the view point of precise controlling of reaction temperature and variably selectivity of the F-T catalyst by hanging operating conditions, reactor system was studied (Samiran, 2007). The summary of reactor studies is summarized in Table 2.2

Table 2.2: F-T synthesis reactors and their main feature, (Samiran, 2007).

Type of reactor	Status	Structural features	Operating Temp. (°C)	Approx. Heat Transfer coefficient (kcal/m^2.hr. °C)	Major product
Old fixed bed (German)	Industrial scale (ohsolate)	Shell & double tube (concentric)	220-260	30	Diesel oil and wax
Improved fixed bed (Arge)	Commercial	Shell & Tube	220-260	150	Diesel oil and wax.
Multi bed	Pilot scale	Shell & Tube and Tray		NA	
Tubular-cum Tray	Pilot scale	Shell & Tube and Tray	220-260	150-170 Tubular section & mainly as sensible heat from Tray	Diesel oil & Wax or gasoline & Diesel oil
Hot gas recycle	Pilot scale	Single catalyst bed (Cylindrical shell)	300-350	*	Gasoline
Oil recirculation	Pilot scale	Single catalyst bed. (Cylindrical shell)	220-270	*	Gasoline
Fixed fluidized bed.	Commercial	Cylindrical shell. Heat transfer through tube bundle in bed.	300-330	450	Gasoline & Chemicals
Circulating fluidized system	Commercial	Cylindrical shell with two cooling zones Top & bottom connected through piping loop	300-330	450	Gasoline & Chemicals
Slurry phase	Commercial	Cylindrical shell. Heat transfer through tube bundle in bed.	200-320	200	Gasoline/ Diesel oil/Eax.